

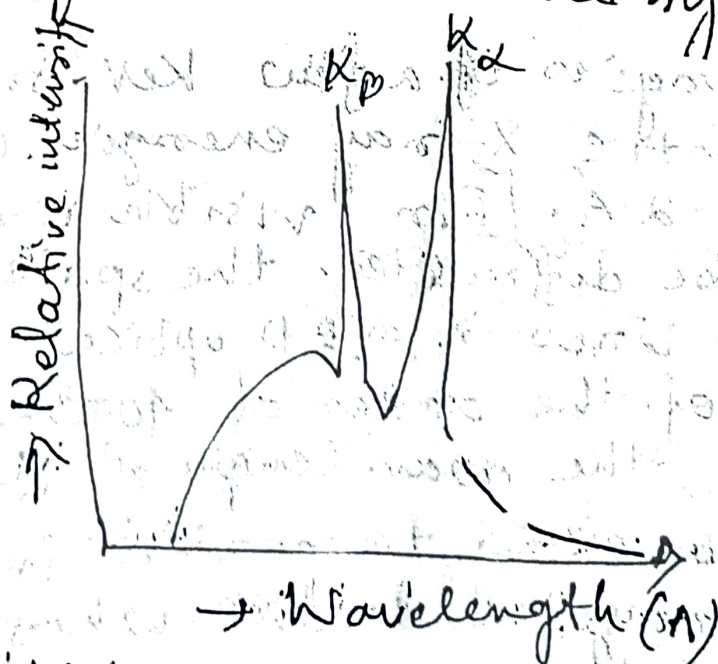
XRD Unit-2 (second part)

(XRD is an experimental technique used to determine the crystal structure and lattice parameters of material systems in bulk and nanoregimes.)

Typical interatomic distances in a solid are of the order of few Angstroms ($1 \text{ \AA} = 10^{-10} \text{ m} = 0.1 \text{ nm}$). An electromagnetic (EM) probe of the microscopic structure of a solid, should have a matching wavelength corresponding to the energy of the order of $E = h\nu = \frac{hc}{\lambda} = \frac{hc}{10^{-10}}$
 $= 12.3 \times 10^3 \text{ eV}$

Energies of a few KeV produce characteristic X-ray energies of wavelength $\sim 1-2 \text{ \AA}$. [For visible e.m. radiation to be diffracted, the spacing between the lines in a 2D optical grating should be of the order of $4000-7000 \text{ \AA}$. Therefore, the wavelength of X-rays $\lambda_{\text{X-ray}} \sim 1-2 \text{ \AA}$ can be used to realize information about the crystal lattice whose dimensions are in the same range as this wavelength range.]

The X-rays emitted by sources made of certain heavy elements (Mo, Cu, Co, Fe, Cr and Zn) consist of a continuous wavelength range (which is termed as white radiation or Bremsstrahlung). The minimum wavelength in the continuous wavelength (λ) spectrum is inversely proportional to the applied voltage that accelerates the electrons towards the target. If the applied voltage is sufficiently high, then in addition to the radiation continuum, a characteristic radiation of a specific wavelength and intensity is also emitted by the target.



Characteristic spectrum of X-rays emitted from a Mo target at 85 kV

X-ray diffraction (XRD) is based on constructive interference of diffracted X-rays by the atoms or ions from successive lattice planes ^{of the sample} which satisfy condition of Bragg's law

$$2d \sin \theta = n\lambda$$

where d = interatomic separation between the lattice planes,

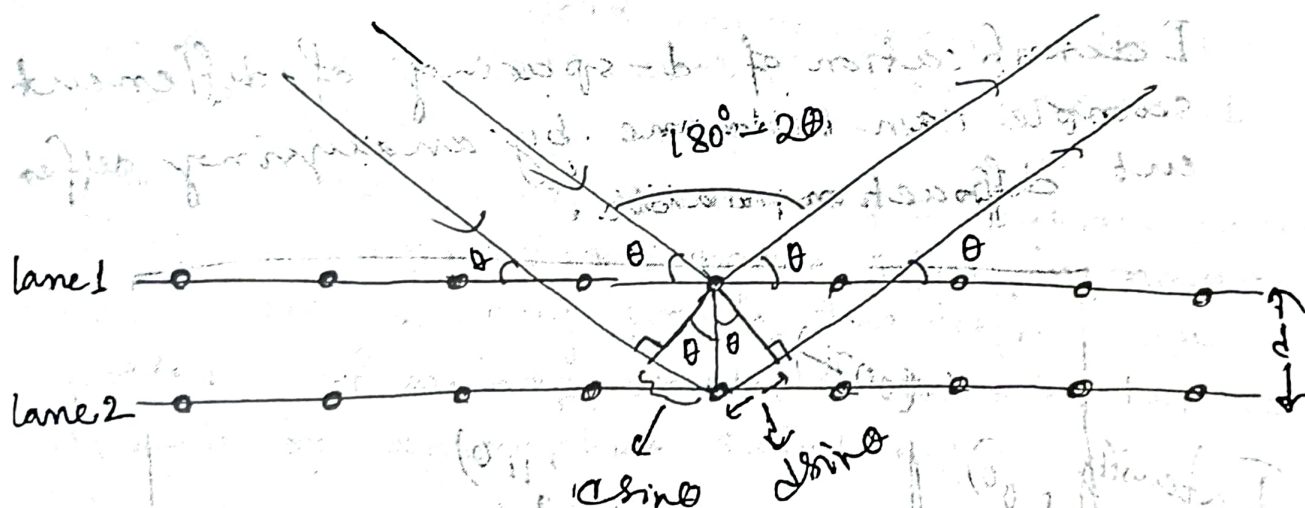


Fig :- X-rays shown specularly diffracted from adjoining planes.

~~N.B~~ Very small λ [$\lambda \sim 0.1 \text{ \AA}$] produces no reflection, it leads to absorption in the process.

This law relates the wavelength of X-ray to diffraction angle and lattice spacing in sample. These diffracted X-rays are detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffracted X-rays can be captured due to random orientation of powder material.

Identification of d-spacing of different sample can be done by analysing different diffraction peaks.

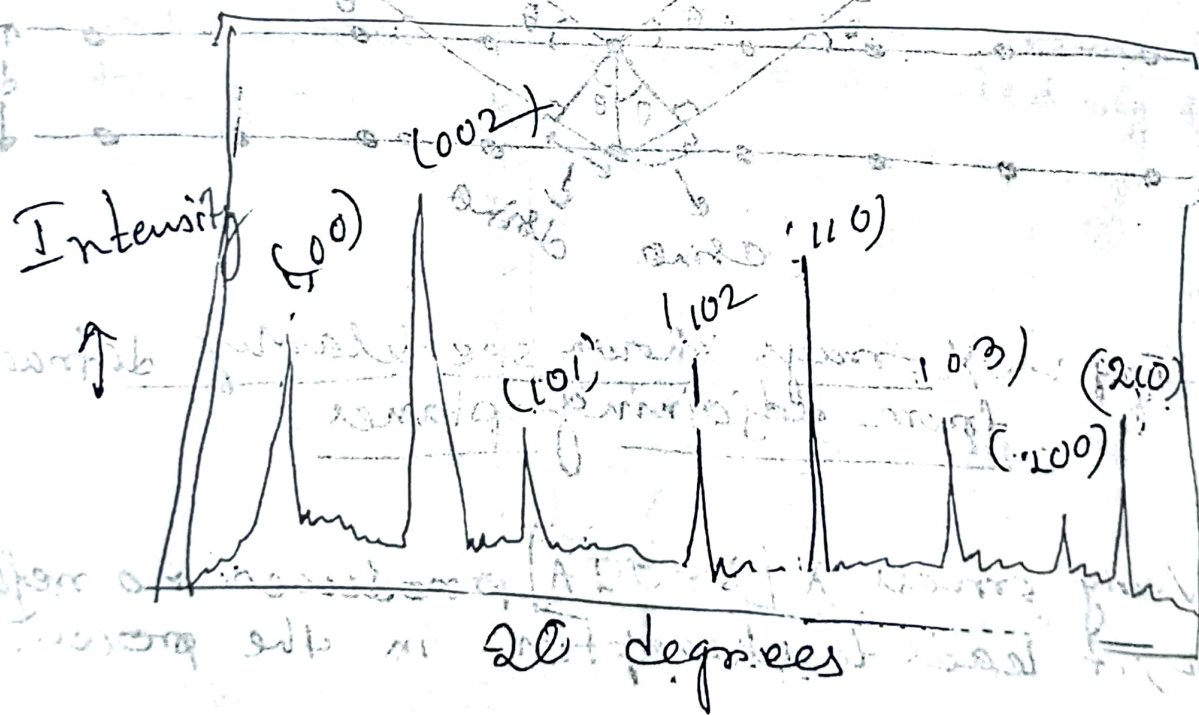


Fig. Shows XRD pattern which indicates random orientation of particles/crystallites in a polycrystalline material.

Structural changes in nanomaterials are known to contain a large number of small single-crystallites with random orientation. In the case of nanoparticles, the particles also have random orientation e.g. In case of gold nanoparticles, the structural properties evolve with size and size shape.

XRD is based on wide-angle elastic scattering of X rays. Since grain size in nanoparticles is very small, the diffraction pattern of nanoparticles looks similar to those of amorphous substances.

Single crystal nanoparticles exhibit size dependent features including slight shifts in the position of Bragg peaks, anomalous peak heights and widths. The peaks show considerable broadening for nanophase materials (particles, clusters, quantum dots etc). The diffraction peaks for well-crystallized materials are very sharp, but for most of the polycrystalline materials, the peaks are broad.

The empirical formula for obtaining the crystalline size is given by

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where λ is the wavelength, β gives the broadening of diffraction line measured at half its maximum intensity in radians and D is the average crystallite size. Line broadening is mainly used to measure the particle size of fine flowing powders.

To find out the parameter β , we mix the material with a standard sample that has a particle size greater than 100 nm. In the diffraction pattern of this mixture, we obtain sharp lines from the standard and broad lines from the test sample. If β_s is the broadening for the standard, β_m is of the material then β is given by

$$\beta^2 = \beta_m^2 - \beta_s^2$$

Another method for determining the particle sizes of nanoparticles. It comes from the diffuse scattering close to the transmitted beam. It helps in size as well as shape determination of amorphous and crystalline materials.

SEM

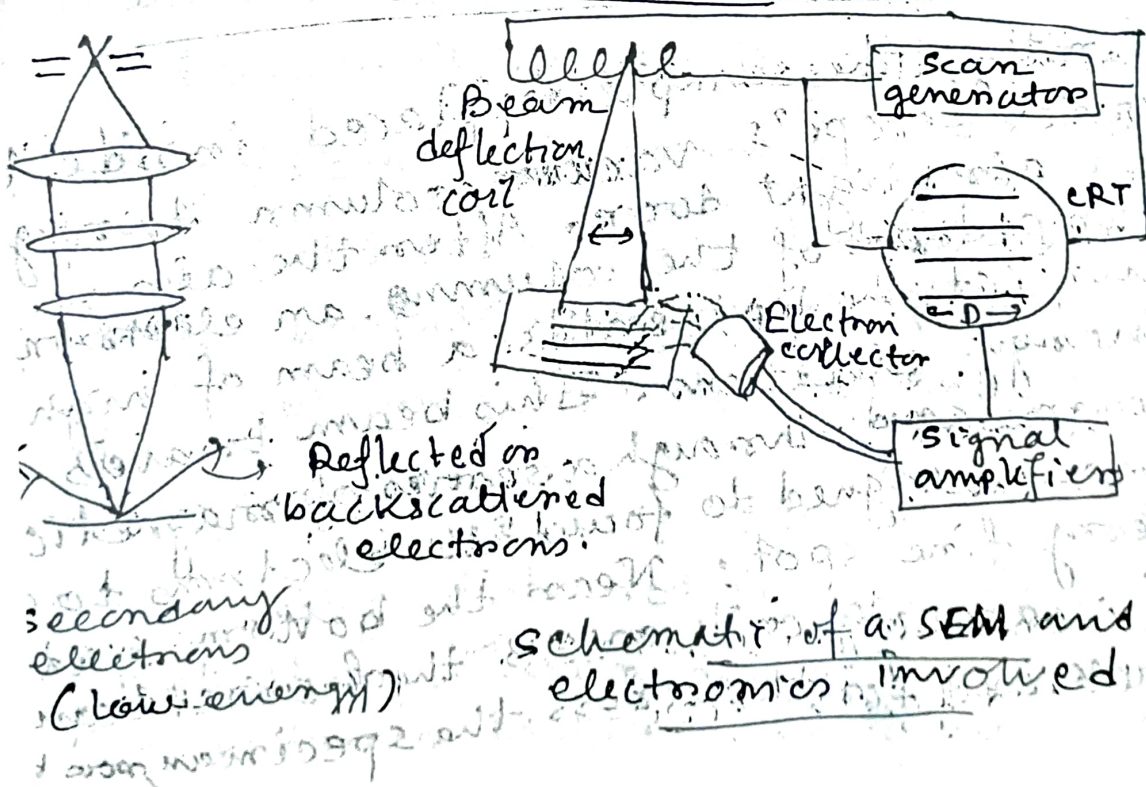
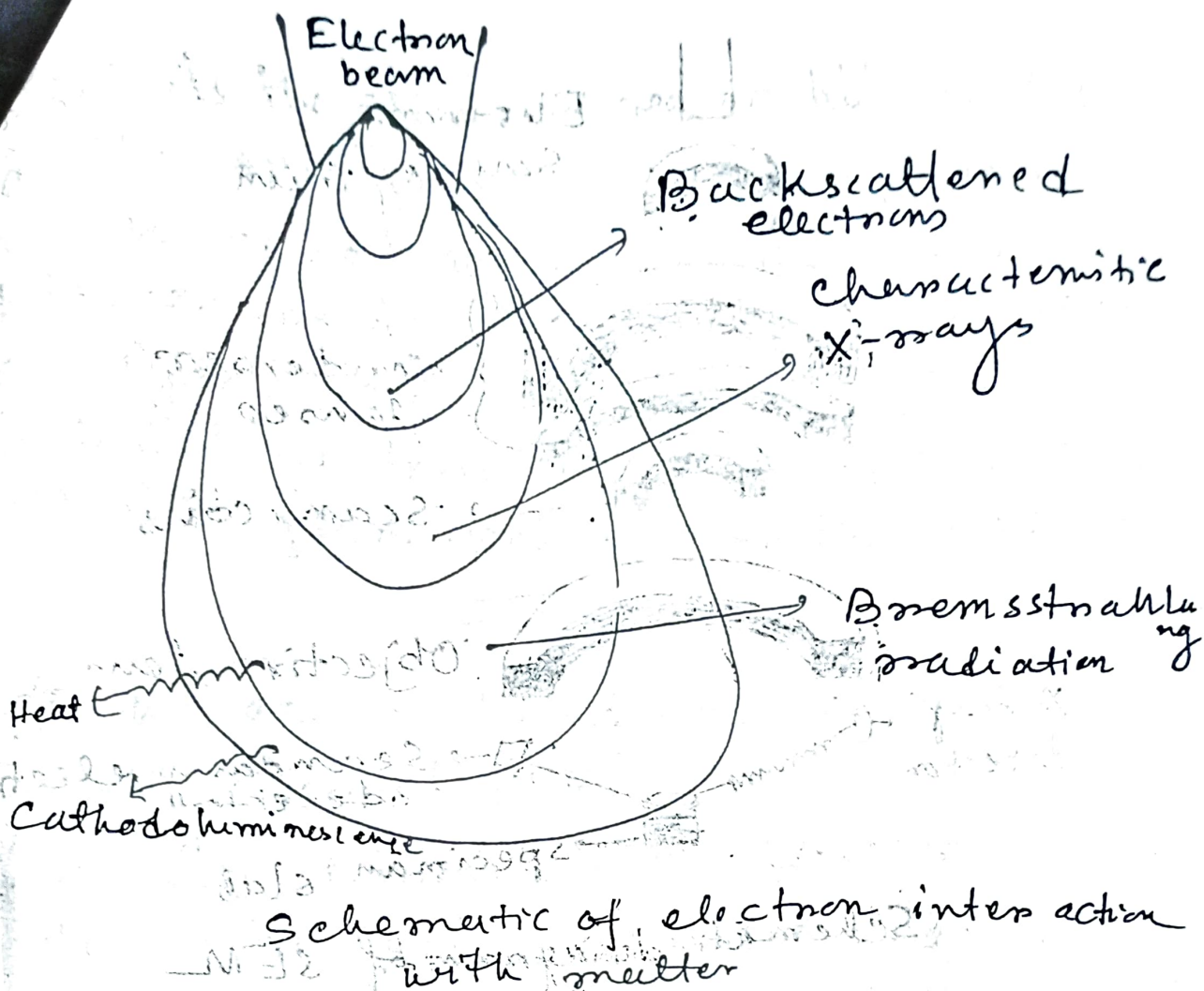
Scanning electron Microscopy

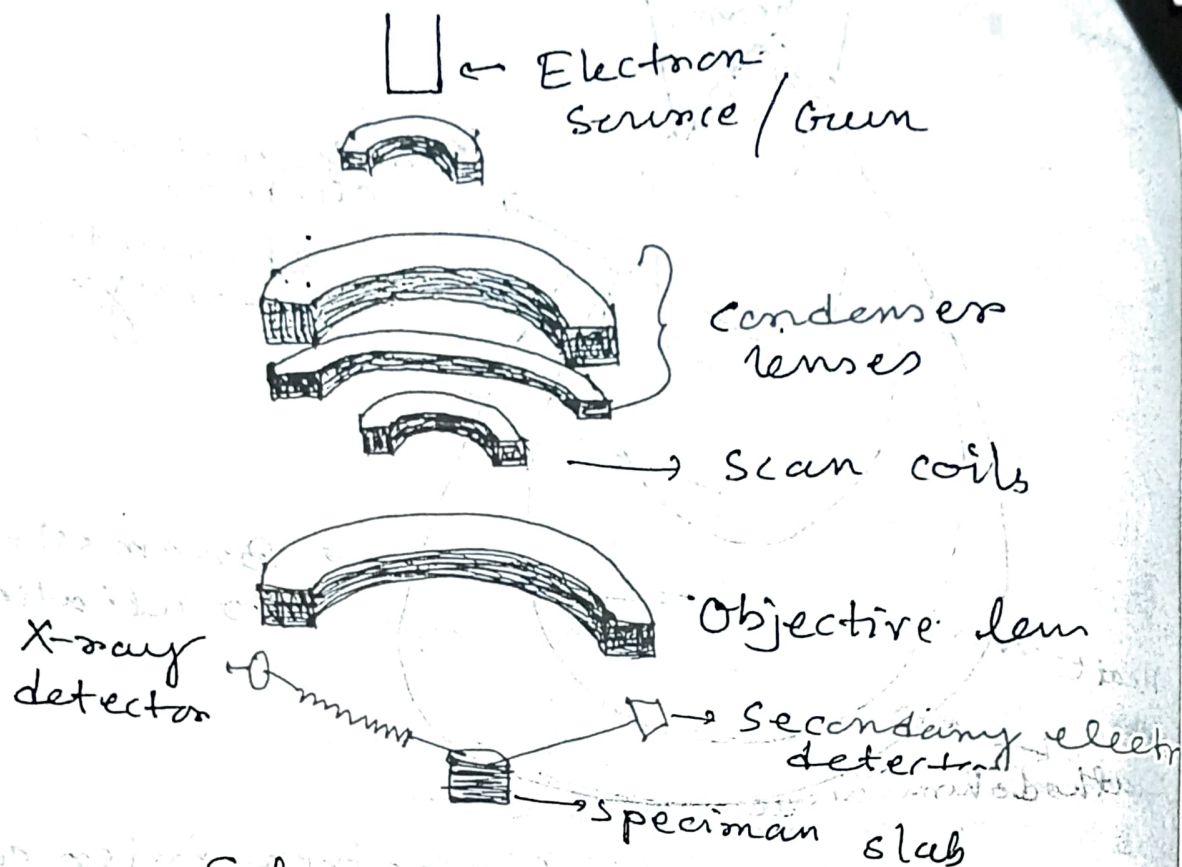
(SEM is an analytical instrument which resolution is less than 1 nm . It is used to study topography, morphology, composition and crystallographic information.)

SEM is a type of electron microscope capable of producing high resolution images of a sample surface. Whole system of SEM must be vacuum protected to prevent scattering of the electrons by stray air molecules and the specimen must absorb or reflect electrons.

SEM consists of virtual source at the top represents the electron gun, producing a stream of monochromatic electrons. The stream is then condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to ~~both~~ form the beam and also to limit the amount of current in the beam. It works in conjunction with the condenser aperture ^(not very selective) to eliminate the high angle electrons from the beam. The beam is then restricted by the condenser aperture eliminating some high angle electrons.

The 2nd condenser lens forms the electron beam into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob". A user selectable objective aperture further eliminates high angle electrons from the beam. A set of coils then scan and sweep the beam in a grid fashion dwelling on points for a period of time determined by the scan speed (microsecond range). The final lens, the objective, focuses the scanning beam onto the part of the specimen desired when the beam strikes the sample and dwells for a few microseconds interaction occurs inside the sample and are detected with various instruments. Before the beam moves to its next dwell point, these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number. (The more the reactions, the brighter the pixel). This process is repeated until grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.





Schematic diagram of SEM

Firstly, the sample is placed inside a microscope's vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun (at the top) emits a beam of high energy electrons. This beam travels downwards through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, now

now. As the electron beam hits each spot on the ~~spo~~ sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample.

What are the advantages of FESEM over Normal SEM?

⇒ In Normal SEM, electrons are thermionically emitted from a filament based cathode and are accelerated towards an anode.

In FESEM, electrons can be emitted via field emission. A cold cathode field emitter, ~~does~~ is used which does not require to heat the filament.

FESEM produces clearer, less electrostatically distorted images with high spatial resolution down to 1 nm. This is 3 to 6 times better than conventional SEM.

Also in FESEM, smaller area contamination spots can be examined at electron accelerating voltages. As a result high quality, low voltage images are obtained with negligible electrical charging of samples.

AFM $\Rightarrow$ measures topography (height, roughness)

The instrument is based on the principle that when a tip is integrated to the end of a spring cantilever, is brought within the interatomic separation between the tip and the sample, interatomic potentials are developed between the atoms of the tip and the atoms of the surface. As the tip moves across the surface, the interatomic potentials force the cantilever to bounce up and down with the change in contours of the surface. Therefore by measuring the deflection of the cantilever, the topographic features of the surface can be mapped out.

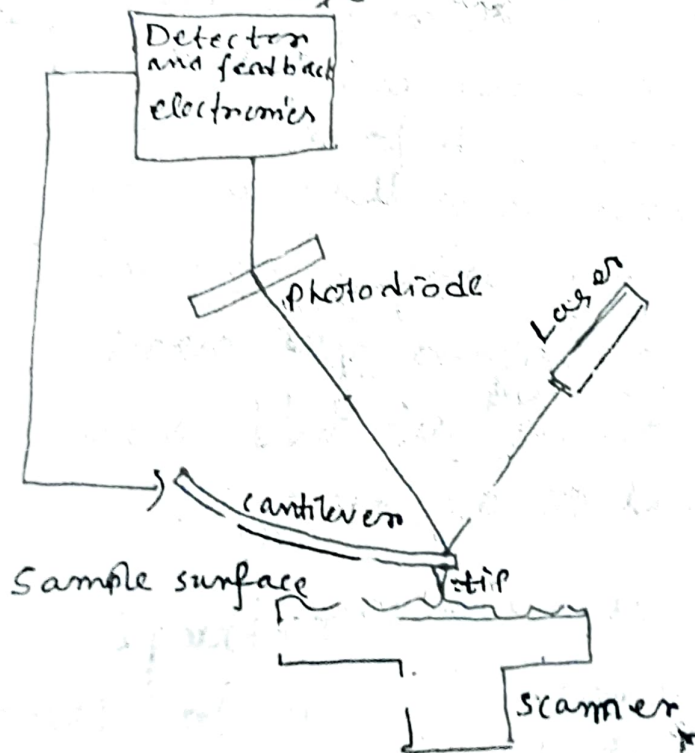
The measured cantilever deflection in AFM apparatus can be detected using a laser beam that is focused on the backside of the reflective coated cantilever and the reflected laser beam intensity is measured using a photo sensitive diode (split photo diode) that in turn allows a computer to generate a map of surface corrugations or morphology or topography.

So ~~the~~ AFM operates by measuring attractive or repulsive forces betⁿ a tip and the sample.

* In repulsive contact mode, a large lateral force can be exerted on the sample as the tip attached at the end of leaf spring or cantilever is dragged over the specimen and some sort of deflection measuring apparatus measures the vertical deflection of the cantilever, which indicates the local sample height. But the forces can ~~deform~~ result in deformation of tip and damaging of sample. This type of microscopy is also called lateral force microscopy (LFM).

* In Tapping mode or noncontact mode, AFM derives topographic images from measurements of attractive forces. Here the tip is ^{not} in constant contact with the surface, the tip makes intermittent contact with the surface. As the tip is scanned over the surface, the cantilever is driven at resonant freq. (hundreds kHz).

because the contact time is a small fraction of its oscillation period and hence the lateral forces can be reduced. Dramatically, tapping mode is usually preferred to image samples with structures that are weakly bound to the surface or samples (polymers, thin films). There are also two types of image contrast mechanisms in tapping mode $\rightarrow$ one is Amplitude imaging and another is phase imaging. In amplitude imaging, the feedback loop adjusts the Z-piezo so that the amplitude of the cantilever oscillation remains constant. The voltage needed to keep the amplitude constant can be compiled into an image.



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Schematic diagram of the operating principle of an AFM

force distance curve

